ITEM NO.: 4
DATE: May 26, 2000
PROPOSAL NO.: 2453-214

STAFF EVALUATION OF AN INTERAGENCY RESEARCH PROPOSAL

TITLE:	Studies of the Atmospheric Chemistry of Volatile Organic Compounds and of their Atmospheric Reaction Products
CONTRACTOR:	University of California, Riverside
PRINCIPAL INVESTIGATORS:	Dr. Roger Atkinson and Dr. Janet Arey
BUDGET:	$299,987
DURATION:	36 Months

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I. SUMMARY

Large quantities of volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic sources. In the atmosphere, these compounds can react with hydroxyl (OH) radicals, nitrate (NO_3) radicals, and ozone (O_3), or can undergo photolysis to form products which typically undergo additional reactions. The reactions of VOCs and their subsequent products can lead to the formation of ozone, secondary organic aerosol (SOA), and toxic air contaminants, resulting in adverse effects on human health and visibility. While the reaction kinetics and mechanisms of the initial reactions of many VOCs are believed to be well understood, much less is known about the subsequent reactions of the products of the initial reactions. To understand the effect of an emitted compound on air quality, it is necessary to have knowledge about both the parent compound and its first and later generation products.

This project will investigate the atmospherically important reactions of the first generation products of selected VOCs. It will address the critical gaps in our understanding of the chemistry of compounds important in the formation of ozone, such

as aromatic compounds, carbonyls, and multifunctional carbonyls. Carbonyl and multifunctional carbonyls are also believed to influence the production of SOA. Another area of investigation will be the formation of nitro-polycyclic aromatic hydrocarbons (PAHs). PAHs, such as naphthalene and biphenyl, can be transformed in the atmosphere to nitro-PAHs, compounds which are more carcinogenic than unsubstituted PAHs. This project will investigate the formation of nitro-PAH as a function of the NO_2 concentration. Lastly, it will investigate the products formed from the gas-phase photooxidation of PAHs present in diesel fuel. The information gained in this project will improve our understanding of the processes involved in the formation of secondary pollutants that pose health risks and degrade California's visibility. The information will be used to improve the chemical mechanisms used in ARB's attainment modeling for the State Implementation Plan. The chemical mechanisms are also necessary for reactivity calculations, which are the basis for ARB's reactivity-based limits for aerosol coatings. Thus, the results of this project will support ARB's use of hydrocarbon reactivity in consumer product regulations.

II. TECHNICAL SUMMARY

Objective

The objective of this proposal is to investigate the reactions of selected first and later generation products. The work will concentrate on carbonyls and multi-functional carbonyls produced by the reactions of alkanes, alkenes, and aromatic hydrocarbons. Additional work will investigate the reactions of aromatic hydrocarbons with OH, the formation of nitro-PAHs, and the photo-oxidation of PAHs found in diesel fuel.

Background

Our knowledge of the chemistry which occurs in the atmosphere is far from complete. This is primarily due to the complex nature of both the mixtures of VOCs emitted to the atmosphere by human activity and the series of reactions that many organic chemicals undergo in the atmosphere before reaching their final products. The need to understand the atmospheric reactions of organic compounds became obvious in the early 1950s, when Dr. Haagen-Smit demonstrated that the reaction of VOCs with NO_x produces O_3 and other organic products. Research in the decades that followed led to an enormous body of knowledge about the chemistry of organic compounds in the atmosphere. As a result, the initial reactions for many classes of VOCs are either reliably known or can be estimated with a reasonable degree of certainty. However, some common classes of compounds, such as aromatics, still have significant uncertainties associated with their mechanisms. For example, while it is known that simple aromatics react with OH radical via addition to the aromatic ring to form OH-aromatic adducts, the mechanisms and products of the subsequent reactions of the adduct with NO_2 and O_2 are uncertain. As a result, the SAPRC-99 chemical mechanism, which is used to calculate reactivity values for ARB's regulations, must rely on a parameterized mechanism that has been adjusted to fit chamber data.

Additionally, for many compounds, the initial reaction is only the first in a long series of reactions that occur before a final non-reactive product is produced. These intermediate products can also react to form O_3, SOA, and, in some cases, toxic air contaminants. Thus, information about the identities, yields, and further reactions of first and later generation products is also necessary. The information acquired in this project will improve our understanding of the chemical mechanisms responsible for the formation of tropospheric ozone. The results will also provide important information about compounds that are believed to be significant contributors to SOA.

Proposal Summary

Previous work has focused on the initial reactions of emitted VOCs. This project will build on that foundation by conducting product and kinetic studies of the first generation products of the initial reactions. The main thrust of the work will be directed at carbonyls and multifunctional carbonyls. These classes of compounds are believed to play an important role in the formation of tropospheric ozone formation, by aiding in the creation and depletion of radical oxidizing species. The polar character of the carbonyl group results in increased activity in biological systems and, thus, these molecules are a probable cause for some of the adverse health effects of particulates. However, until recently, these molecules could not be studied, due to the lack of a suitable analytical technique. This project will address this significant gap in the understanding of atmospheric chemistry.

As mentioned above, the reactions of aromatic compounds still have significant uncertainties associated with them. This project will investigate the reactions of the first intermediate of the reaction of simple aromatics with OH radical, the OH-aromatic adduct. It will also examine the reactions of more complex aromatic systems, PAHs by studying OH-PAH adducts. Additionally, it will produce detailed mechanistic and kinetic data on the formation of nitro-PAHs.

Specific tasks included in this proposal are:

- Investigation of the atmospheric chemistry of selected first-generation products formed from the atmospheric degradation of alkanes, alkenes, and aromatic hydrocarbons.
- Quantification of the dihydroxycarbonyls formed from the reactions of OH radical with > C_5 alkenes in the presence and absence of NO_x.
- Product studies for the reactions of selected carbonyl compounds.
- Product studies for the reactions of alkenes with NO_3 radicals and ozone.
- Investigation of the products of the gas-phase reactions of OH radical with aromatic hydrocarbons in the presence and absence of NO_x.
- Investigation the reactions of selected OH-PAH adducts with O_2 and NO_2 and the formation of nitro-PAH from the OH radical and NO_3 radical-initiated reactions.
- Investigation of the products formed from the gas-phase photo-oxidation of PAHs present in diesel fuel. Bioassay-directed chemical analysis will be used to identify which of the products are mutagenic.

The work in this project will take full advantage of the impressive array of analytical instrumentation available at the Air Pollution Research Center (APRC). The APRC has three large environmental chambers. One of the chambers is interfaced with an atmospheric pressure ionization tandem mass spectrometer and a second chamber contains a multiple reflection optical system interfaced to a Fourier transform infrared spectrometer (FTIR). Other analytical instrumentation available includes nine gas chromatographs with a variety of detectors, including flame ionization, electron capture, FTIR, and mass spectrometers, two high pressure liquid chromatographs, and NO_x and O_3 analyzers. The investigators plan to use multiple chambers and analytical methods for each reaction studied, since they have found that the maximum amount of information can be obtained in this manner. The bioassay testing laboratory necessary to perform mutagenicity testing is also available at APRC.

III. STAFF COMMENTS

Staff from Stationary Source, Planning and Technical Support, and Research Divisions reviewed this proposal and had very positive responses. The principal investigators (PIs), Drs. Atkinson and Arey, have years of experience in investigations of the atmospheric chemistry of VOCs. They have published numerous articles on the gas-phase reactions of alkanes, alkenes, aromatic compounds, and oxygenated compounds. They are recognized experts on atmospheric chemistry and have a proven record of successful studies. Their experience guarantees that the results from the proposed study will be accurate and relevant. The PIs have worked on several ARB-sponsored projects in the past and have always delivered quality results with a very reasonable budget. In summary, the knowledge and experience of the investigators and the experimental equipment and analysis tools available for the proposed study ensure that the study would generate useful, quality results.

Accurate and complete information about the chemical reactions which occur in the atmosphere is essential to achieving ARB’s goal of effective and efficient reduction of air pollution. Specific details as to the products, yields, and reaction kinetics of specific organic compounds are vital to the development of effective control strategies. As ARB expands its areas of concern to include PM2.5, and thus secondary organic aerosols, and seeks to address increased public concern about air toxics, specific knowledge about the sources and reactions of compounds of interest is needed. This information can only be generated through studies of basic atmospheric chemistry. Additionally, the information produced as a result of this proposal is necessary for a state-of-the-science modeling program that evaluates ozone impacts from reactions of individual consumer product compounds, as well as attainment planning work that utilizes reactivities of all VOCs together. Additionally, the formation of secondary organic particulate matter will be important in future modeling for PM attainment plans.

IV. STAFF RECOMMENDATION

Staff recommend the Research Screening Committee approve this proposal for a total amount not to exceed $299,987, subject to inclusion of appropriate additions and revisions in response to the staff comments, and any changes and additions specified by the Committee.